Recent progress in melt-processed (Nd–Sm–Gd)Ba$_2$Cu$_3$O$_y$ superconductors

M. Muralidhar *, S. Nariki, M. Jirsa 1, N. Sakai, M. Murakami

Superconductivity Research Laboratory (SRL), International Superconductivity Technology Center, 1-16-25 Shibaura, Minato-ku, Tokyo 105, Japan

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Abstract

We have prepared (Nd,Sm,Gd)Ba$_2$Cu$_3$O$_y$ “NSG-123” with various contents of (Nd,Sm,Gd)$_2$BaCuO$_5$ “NSG-211” or Gd$_2$BaCuO$_5$ “Gd-211” with the aim of optimizing flux pinning. Microstructure observed by transmission electron microscopy exhibited a high density of RE-rich RE$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ (RE-123ss) clusters with their size and dispersion depending on the initially added 211 content. Gd-211 10 mol% distributed as small clusters ranging from 3 to 10 nm in size enhanced pinning at intermediate fields. The magnetization measurements suggested that the optimum oxygen pressure during melt-growth process for this system was around 1% pO$_2$. It was confirmed that this material can be grown into single domain more than 40 mm in diameter.

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1. Introduction

Recent progress in melt-processing of bulk high-temperature superconductors (HTSC) has created a basis for various engineering applications. For majority of power applications high critical current density ($J_c$) and high irreversibility field ($H_{irr}$) are of main interest. With respect to the cost for refrigeration, the most interesting temperature for such applications is 77.3 K, the boiling temperature of liquid nitrogen. Therefore, high $J_c$ and $H_{irr}$ at this rather high temperature are highly desired.

It is well known that melt-textured process is the most eminent technique used for preparation of bulk high-temperature superconducting materials, leading to superior transport and magnetic properties [1–3]. Melt-textured LRE-Ba$_2$Cu$_3$O$_y$ “LRE-123” systems (LRE: light rare earth) with three LRE elements on the RE site commonly possess superior flux pinning at 77 K [4–6]. Recently, we showed that (Nd$_{0.33}$Sm$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$ “NSG-123” exhibits strong flux pinning at 77 K up to 2 T ($H||c$-axis). The TEM-EDX analysis identified the

* Corresponding author. Address: Superconductivity Research Laboratory (SRL), ISTEC, Division 3, 3-35-2, Isoka-Shinden, Morioka, Iwate 020-0852, Japan. Tel.: +81-19-635-9015; fax: +81-19-635-9017.
E-mail address: miryala1@istec.or.jp (M. Muralidhar).
1 Present address: Institute of Physics ASCR, CZ-182 21 Praha 8, Czech Republic.
source of the pinning as microscopic chemical fluctuation in the superconducting matrix on nanometer scale [7]. Like in other melt-textured RE-123 materials, pinning at low fields can be controlled by secondary phase particles (SPP). These rather large normal particles probably also induce the formation of point-like defects (e.g., strains, stacking faults etc.) in their vicinity and, as a result, indirectly participate also on the pinning enhancement at intermediate and high fields. The characteristics for these compounds are not only the excellent magnetic properties at high temperatures but also a uniform microstructure and a good reproducibility.

The present work aimed at optimizing flux pinning of the NSG-123 system at 77 K. We add a variety of SPP, and employed different gas atmospheres during the melt-growth stage and studied $J_c\sim B$ performance at liquid nitrogen temperature. We also attempt to grow a large grain NSG-123 superconductor using the top-seeded melt-growth technique.

2. Experimental

High-purity commercial powders of Nd$_2$O$_3$, Sm$_2$O$_3$, Gd$_2$O$_3$, BaCO$_3$ and CuO were weighed to have a nominal composition of (Nd$_{0.33}$Sm$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$. The starting powders were thoroughly ground, calcinated at 880 °C for 24 h with intermediate grinding, and finally pressed into pellets. The sintering was carried out at 910 °C for 15 h. This process was repeated three times under low oxygen partial pressure. Commercial high pure Gd-211 or NSG-211 (<3 μm) powders with the volume fractions of 10–50 mol% were added before pressing and sintering, together with 0.5 mol% of Pt and 1 mol% CeO$_2$ to reduce the size of the RE-211 particles. The pellet diameter was 20 and 15 mm in thickness. In the process of preparation of large bulk samples (30–40 mm in diameter), we also added 20 wt.% silver oxide to improve the mechanical strength of the NSG-123 material. The pellets were compressed with cold isostatic pressing (CIP) under the pressure of 2000 kg/cm$^2$. The melt-textured NSG-123 samples were grown in a tube furnace using the OCMG process combined with a top-seeded melt-growth technique. Details of the heat treatment were described in Ref. [8]. Several sets of samples were prepared in 1% and 0.1% $p$O$_2$/Ar with a gas flow rate at about 300 ml/min.

For oxygen annealing, small specimens with dimensions of 1.5×1.5×0.5 mm$^3$ were cut from the as-grown crystals and annealed in flowing O$_2$ gas in the temperature range of 325–600 °C with the following heat treatment schedule. The samples were heated to 600 °C with the rate 300 °C/h, held there for 1 h, cooled down to 500 °C at the rate 8 °C/h, then to 400 °C at the rate 4 °C/h, and finally to 325 °C at the rate 1.5 °C/h, held there for 150 h, and subsequently cooled down to room temperature. SQUID measurements on the oxygenated samples showed that $T_c$(onset) varied between 93 and 94.1 K.

Microstructure was studied by means of transmission electron microscope (TEM) and high resolution electron microscope (HREM). Magnetization hysteresis loops (MHL's) were measured mainly at 77 K in applied fields up to 7 T using a commercial SQUID magnetometer (Quantum Design, model MPMS7), for which the scan length was 1 cm to minimize field inhomogeneity. The external magnetic field was always applied parallel to the c-axis of the sample. The magnetic $J_c$ values were estimated using the extended Bean’s critical state model [9].

3. Results and discussion

Fig. 1 presents top surface images of two OCMG-processed NSG-123 samples with 30 mol% Gd-211 and 20 wt.% of silver oxide. The sample diameters were around 30 and 40 mm. Nd-123 seed is clearly seen on the top surface. The trapped field measurements also confirmed the single cone shape profile (see in Fig. 2) reflecting the single domain. It is interesting to note that at applied fields of 0 and 2 T, trapped fields of 1.2 T
(remnant state) and 1.5 T (3.5 T at the peak) were achieved in 30 mm in diameter sample at 77 K. Evidently, NSG-123 pellets of larger diameters can trap even higher fields. A large grain size is critical for achieving high trapped-fields in bulk superconductors.

Earlier microscopic studies of NSG-123 samples with various contents of Gd-211 [7] showed mostly round and uniformly dispersed SPP. TEM observation showed a uniform dispersion of fine round particles for the sample with more than 20 mol% of the secondary phase. TEM-EDX analysis clarified that larger particles consisted of Nd, Sm, and Gd on the RE site in different ratios. The small round particles were mainly "pure" Gd-211. Since no such particles were added to the system, they must have been produced during the melt processing. Their portion reflected the initial quantity and type of the added secondary phase. It is known that the critical current density is inversely proportional to the particle size [11], hence the Gd-211 particles are particularly important for the enhancement of the low-field critical current densities.

Fig. 3(a) and (b) presents the TEM dark-field micrographs of NSG-123 samples with 10 and 30 mol% Gd-211. The white and black regions in Fig. 3 reflect the compositional fluctuation induced by LRE/Ba substitution, white colour corresponding to RE-rich areas as recognized by TEM with EDX analysis. The size of the RE-rich clusters ranged from 3 to 10 nm, however, in the case of 30 mol% Gd-211, the cluster size was 5–20 nm.

Fig. 4 presents the field dependence of the critical current density, $J_c(H_a)$, of NSG-123 samples containing NSG-211 particles in different amounts. The $J_c$ values were determined from magnetic measurements performed at liquid nitrogen temperature (77 K) for $H || c$-axis. All the samples were melt-processed in Ar–1% $p\text{O}_2$ atmosphere. It is evident that the shape of the $J_c(H_a)$ curves depends on the amount of initially added NSG-211 phase. At around zero applied field (self-field), the $J_c$ values systematically increased with increasing NSG-211 concentration. With increasing applied field the contribution of pinning on large particles rapidly decayed and was replaced by pinning on other types of defects. The $J_c$ values at the
secondary peak position for the samples with 10, 20, 30, and 40 mol% of NSG-211 were 75, 49, 47, and 47 kA/cm², respectively, and the respective peak fields were 2.2, 2.6, 2, and 2 T. We see that in high fields the correlation between $J_c$ and SPP content is quite different from that in low fields: the highest pinning (at the secondary peak) corresponds to 10 mol% of NSG-211.

For the NSG system with initially added Gd-211 particles the same analysis as above [7] is presented in Fig. 5. The highest $J_c$ value of 100 kA/cm² at the peak field of 2 T ($H||c$-axis) was obtained for 10 mol% of Gd-211. This is the highest value at a non-zero field reported so far for melt-processed LRE-123 bulk superconductors. Pronounced secondary peaks were also observed in the samples with 20, 30 and 40 mol% Gd-211 (76, 80, and 72 kA/cm², respectively), always significantly higher than those with the same amount of NSG-211. Again, the $J_c$ values below 0.3 T systematically increased with increasing Gd-211 concentration, a similar trend as observed in the sample with NSG-211. On the other hand, $H_{irr}$ and $J_c$ values at 3 and 4 T were relatively low for 30 and 40 mol% of Gd-211, probably due to an improper chemical ratio of the NSG-123 matrix, which is similar to the NEG123 system [12].

Fig. 6 presents $J_c(H_a)$ curves of the NSG-123 samples containing Gd-211 SPP in different amounts, melt-processed in Ar–0.1% $pO_2$. As in the previous cases, the $J_c$ values at zero field and 0.3 T increased with increasing Gd-211 content. However, the critical current density values were lower for all Gd-211 contents compared to the samples.
prepared in Ar–1% $pO_2$ atmosphere (Fig. 5). No significant change was observed in a peak position and the irreversibility field. These results imply that the optimum oxygen pressure for this system is around 1% $pO_2$.

4. Summary

Large c-axis oriented NSG-123 bulk samples of 40 mm diameter were fabricated using the OCMG process combined with a top-seeding technique. Transmission electron microscopy confirmed that the size and dispersion of the clusters arising from the chemical fluctuation were strongly affected by the initially added amount of the secondary phase. The magnetization measurements on NSG-123 samples with a variety of SPP contents produced in different low oxygen atmospheres showed that $J_c$ at self-field, was improved with increasing the secondary phase like in NEG-123 system.

In all the cases $J_c$ at zero field (self-field) and 0.3 T increased with increasing amount of NSG-211 or Gd-211. Fine Gd-211 particles were more efficient in enhancing pinning both at low and intermediate fields than NSG-211. The optimum oxygen concentration was for different composites, which was 1% $pO_2$ for the NSG-123.

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